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INTERNATIONAL APPLICATION NO.

PCT/JP99/01429

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PRIORITY DATE CLAIMED

27 March 1998

TITLE OF INVENTION

A METHOD FOR FORMING A FILM

APPLICANT(S) FOR DO/EO/US

Tomo UENO, Tokyo, JAPAN

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
 2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
 3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
 4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
 6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
 7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
 8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
 10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern document(s) or information included:
11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
 13. ☒ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
 14. ☐ A substitute specification.
 15. ☐ A change of power of attorney and/or address letter.
 16. ☒ Other items or information:
 - a. PCT/RO/101
 - b. PCT/IB/301
 - c. PCT/IB/304
 - d. PCT/IB/306
 - e. PCT/IB/308
 - f. PCT/IB/338
 - g. PCT/IPEA/409
 - h. WO99/50899 (cover page)
 - i. International Search Report (with English translation)

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TOKYO UNIVERSITY OF AGRICULTURE

Applicant or Patentee: & TECHNOLOGY Attorney's
Serial or Patent No.: 09/646,988 Docket No.:
Filed or Issued: September 26, 2000
For: A METHOD FOR FORMING A FILM

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) and 1.27(d)) - NONPROFIT ORGANIZATION

I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:

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ADDRESS OF ORGANIZATION 3-8-1, Harumi-cho, Fuchu-shi, Tokyo 183-8538 JAPAN

TYPE OF ORGANIZATION

- ☒ UNIVERSITY OR OTHER INSTITUTION OF HIGHER EDUCATION
☐ TAX EXEMPT UNDER INTERNAL REVENUE SERVICE CODE (26 USC 501(a) AND 501(c)(3))
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(NAME OF STATE _____)
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METHOD FOR FORMING A FILM

by inventor(s) Tomo UENO
described in _____
☐ the specification filed herewith
☒ application serial no. 09/646,988, filed September 26, 2000
☐ patent no. _____, issued _____

I hereby declare that rights under contract or law have been conveyed to and remain with the nonprofit organization with regard to the above-identified invention.

If the rights held by the nonprofit organization are not exclusive, each individual, concern or organization having rights to the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who could not qualify as an independent inventor under 37 CFR 1.9(c) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e). *NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to the status as small entities. (37 CFR 1.27)

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NAME OF PERSON SIGNING Isoshi KAJII

TITLE IN ORGANIZATION President
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SIGNATURE Isoshi Kajii DATE October 5, 2000

09246988-111600

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Tomo UENO

Group Art Unit:

Serial No.: New Application

Filed: September 26, 2000

Examiner:

For: A METHOD FOR FORMING A FILM

PRELIMINARY AMENDMENTCommissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified application,
please enter the following claim changes as noted below:

IN THE CLAIMS:

Claim 4, line 1, delete "any one of claims 1 to 3" and insert
therefor --claim 1--.

Claim 5, line 1, delete "any one of claims 1 to 4" and insert
therefor --claim 1--.

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REMARKS

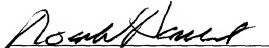
This Preliminary Amendment is submitted to eliminate multiply dependent claims from the above-identified application.

Claims 1-11 are pending herein.

Prompt and favorable examination of this application on the merits is respectfully solicited.

Respectfully submitted,

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September 26, 2000
Date

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(rev. 3/3/00)

7/PRTS

Specification

A METHOD FOR FORMING A FILM

(Technical field)

This invention relates a method for forming a film.

(Background art)

A film-forming technique plays an important part in development of a material and a device. In the recent very large integration taking advantage of a microfabrication technique, it is desired to establish a new film-forming technique particularly in an electronic device such as a ULSI. Up to now, the CVD methods, in which all the constituting elements of a film to be formed on a substrate are supplied from an external atmosphere or the thermal oxidizing method in which elements from an external atmosphere are reacted with constituting elements of a substrate to form a film, have been mainly used. In both of the above methods, now, the elements from the external atmosphere are introduced into a vacuum vessel in molecularity.

The recent miniaturization of an elemental device restricts its film-forming process, particularly requiring to lower its processing temperature. One of the factors to make higher the processing temperature is that the constituting elements from the external atmosphere are supplied in molecularity. That is, a part of atoms constituting the molecular elements to be supplied or dissociated atomicity elements from the molecular elements are essentially required in the film-forming process. The conventional film-forming technique dissociates the supplied molecular elements near a heated substrate, so requiring the energy of the dissociation for the temperature of the heated substrate for. Therefore, it has its limit by itself in lowering of the film-forming process.

In the above film-forming technique of supplying the constituting

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elements from the external atmosphere and depositing the elements on the substrate, for lowering the processing temperature, a sputtering method or a plasma CVD method, in which a given plasma is employed, is suggested and practically used in a part of the film-forming process. The former method etched a solid target by using a plasma energy and deposits the etched particles on a given substrate and the latter method dissociates raw material gas to be supplied and deposits the dissociated elements on a given substrate. These methods are prevailing in solving the above problem, in the view of supplying in advance dissociated elements from the raw material gas onto the given substrate.

On the other hand, a thermal oxidizing process of a silicon substrate, which is typical in the above method of reacting the elements supplied from the external atmosphere with the constituting elements of the substrate, have been widely used in the forming process of gate oxide films of MOSFETs. In the thermal oxidizing process, the gate insulating films having good qualities can be easily formed by heating and holding the silicon substrate at 800°C and over under an oxidizing atmosphere (oxygen molecule-atmosphere). The obtained silicon oxide film is generally called as a "thermally oxidized film". The above method is described in "J.Appl.Phys", p3770, No. 36 (1965), by B.E.Deal and A.S.Grove, and "Quick Reference Manual for Silicon Integrated Circuit Technology" by W.E.Beadle, J.C.C Tsai and R.D.Plummer, published by "John Wiley & Sons Co.(1985), etc. The main reason of using the high temperature and the large excited energy process is that the silicon oxide film/silicon substrate-boundary surface exhibits good electric characteristics.

Although many methods to form the silicon oxide film on the silicon substrate at a low temperature such as the sputtering method or the plasma CVD method as a directly depositing method, are made an attempt,

generally, they shows extremely low boundary face-level density (Dit) which is a typical reference mark for the boundary face characteristic. The reason is that the dangling bonds near the silicon substrate surface, which directly influence the Dit, remain after the silicon oxide film/silicon substrate-boundary face is formed. The part of the dangling bonds may be terminated by hydrogen atoms in a CVD method, but the silicon atom/hydrogen atom-bonds are often cut easily at the ensuing process requiring a temperature of about 400°C. Accordingly, the low temperature-forming method of the silicon oxide film lacks a long-term reliability and has trouble with being applied to forming gate oxide films of LSIs.

Moreover, the method of directly introducing elements dissociated in a plasma atmosphere from an external atmosphere and reacting the dissociated elements with the constituting atomic elements of a substrate is made an attempt to lower the processing temperature. However, it is known, when many molecules each composed of plural atoms are introduced in a plasma, the plasma has an extreme wide energy distribution and thus, the molecules are transformed into a variety of activated species including molecular ions. The thus obtained film does not have its good quality, so that the above method is almost never employed in forming the gate oxide films of MOSFETs requiring harsh conditions.

In addition to the silicon oxide material, a silicon nitride material may be used for the gate oxide film or a passivative film which is insulating film. The silicon nitride film is formed by a variety of methods as in the silicon oxide film. In the case of forming the gate oxide film of the silicon nitride, since the film undesirably has many boundary face-level at its silicon/silicon nitride-boundary face, the film is generally formed so as to have a silicon/silicon oxide/silicon nitride-boundary face.

Recently, a successive process in forming an elemental device

requires low temperature process intensely. To comply with the request, the lowering technique of the processing temperature is desired in the whole film-forming process.

In these years, the miniaturization of the MOSFETs and the lowering of the voltage of a driving power supply reach their limits, so that the conventional thermally oxidized film can not give the MOSFETs sufficient qualities. One of the reasons occurs from the high temperature thermal treatment at 800°C for several ten minutes. That is, when the miniaturization requires to control the impurity-profiles of the MOSFET semiconductor precisely within their shallow profiles, the high temperature thermal treatment destroys the precise shallow impurity-profiles. As mentioned above, the CVD method or the sputtering method not requiring the high temperature thermal treatment degrades the insulating characteristics and the boundary face-qualities because of many dangling bonds. As a result, the miniaturization of the MOSFETs can not tolerate the high temperature thermal treatment, so that the insulating film having good qualities can not be obtained.

Besides, there is a problem due to the environmental change around the MOSFETs. The use of a wafer having a large size for developing productivity has to satisfy the uniformity of the characteristics in all the MOSFETs entirely on the wafer surface. In the case of forming oxide films in a large size equipment corresponding to the large size wafer by using the conventional thermally oxidizing method, the relatively large activation energy of about 1.1 eV to oxidize the wafer surface changes the rate of reaction due to the temperature fluctuation during the heating. It means the difficulty in obtaining oxide films having their uniform thickness on the wafer. When complex calculations are carried out by increasing the number of the MOSFET per one chip, the fluctuation of the characteristics in the MOSFETs

becomes not tolerated and severe. Therefore, the insulating films having uniform characteristics has to be formed for many MOSFETs on the wafer.

The adoption of the insulating film formed at a low temperature for the gate oxide film requires to reduce its Dit value, but now, the high temperature process is required for maintaining the electric characteristic of the gate oxide film. Although the high temperature- and large activation energy-process have been used for giving preference to the electric characteristics under the conditions of the use of a small size wafer and not proceeded microfabrication, a low temperature- and small activation energy-process is required for more miniaturization and enlarging the wafer size without the electric characteristics.

For realizing the low temperature in the film-forming process, it is conceivable to dissociate the molecular elements constituting the film in atomicity and supply the dissociated elements. On the other hand, the molecular elements, if they have their excited energy states from their ground states as their molecularity states, have their excited states maintaining their molecularity states (molecular excitation- state), their ionized states maintaining their molecularity states (molecular ionization-state) and their dissociated states perfectly in atomicity (atomicity-state). When an energy is supplied to the molecular elements from a plasma, they have the above states by low energy turn. Accordingly, when the molecular elements are excited to the atomicity-state, for example, they necessarily have another low energy state. Moreover, when they have large energy to be excited to the atomicity-state, they are almost never excited to the atomicity-state.

(Description of the Invention)

According to the dissociating method of the molecular elements to the atomicity elements, inert gas molecules absorb an plasma energy in advance and have their large quasi-stable level energies, thereafter, giving

their energies to the molecular elements, so that the molecular elements are directly excited to a higher energy states and are easily dissociated to the atomicity elements.

In the case of producing atomicity oxygen elements by dissociating the oxygen molecules with a supplied energy, the oxygen molecules has the states of O^2P , O^1D , O^3S and so on by low energy turn. Since the oxygen molecules at each state has different activation degree, respectively, if adopted for various oxidizing reaction, it is expected that the molecules exhibits different oxidizing velocity and mechanism. If the inert gas molecules having the various quasi-stable state energies collide with the oxygen molecules to generate a plasma, the kind of the atomicity oxygen elements to be generated in the plasma may be controlled.

For dissociating the molecular elements to the atomicity elements, the inert gas molecules, not the molecular elements, absorb the plasma energy, and thereby, the useless excitations of the molecular elements are suppressed. Thus, the inert gas is introduced by the amount equal to or more than that of the molecular elements and thereby, the atomicity elements are effectively produced from the molecular elements.

In a method for forming an insulating film of the present invention, molecular silicon compound elements constituting the insulating film are introduced on a substrate surface in atomicity. The atomicity is carried out by the emission energies of the inert gas molecules absorbing the plasma energy higher than the energy required in the atomicity. Accordingly, the molecular elements are directly excited to the atomicity-state beyond the molecular excitation-state and the molecular ionization-state. The silicon substrate is oxidized as the molecular elements are oxygen molecules and is nitrided as the molecular elements are nitrogen molecules. The reactions have low activation energies, so that they are easily performed on the silicon substrate

surface, not depending on the difference in their reaction temperatures on the substrate. Moreover, since the reactions cut the silicon-silicon bonds and generate the silicon-oxygen bonds or the silicon-nitrogen bonds repeatedly, the thus obtained insulating film/silicon substrate-boundary face has little dangling bonds and low boundary face-level density and thus, the insulating film having excellent insulating characteristics can be formed on the silicon substrate. Consequently, the insulating film having excellent uniform characteristics can be formed on the silicon substrate at a low temperature.

(Brief Description of the Drawings)

For better understanding of the present invention, reference is made to the attached drawings, wherein

Fig. 1 is a structural view of a film-forming equipment in dissociating one kind of molecular elements into their atomicity elements,

Fig. 2 is a view for explaining the energy states and the light emission due to the state-transitions of helium molecule (He) and hydrogen molecular element (H_2),

Fig. 3 is a view showing the emission spectrum of the hydrogen molecular elements when the helium gaseous molecules are introduced,

Fig. 4 is a structural view of a film-forming equipment in dissociating three kinds of molecular elements into their atomicity elements,

Fig. 5 is a structural view of a film-forming equipment in using three kinds of raw material gases and one kind of atomicity-dissociated molecular elements,

Fig. 6 is a structural view of a film-forming equipment in using one kind of raw material gases and one kind of atomicity-dissociated molecular elements,

Fig. 7 is a structural view of a film-forming equipment in using two kinds of atomicity-dissociated molecular elements,

Fig. 8 is a view showing the emission spectrum of the hydrogen molecular elements when the helium gaseous molecules are introduced by the amount equal to or more than the amount of the hydrogen molecular elements,

Fig. 9 is a schematic sectional view of a silicon substrate in which the insulating film has openings in the source and drain areas, and

Fig. 10 is a schematic sectional view of an isolated silicon substrate.
(Best mode for carrying out the present invention)
[A preferred first embodiment in the present invention]

The invention will be described in detail hereinafter, with reference to the attaching drawings.

Fig. 1 is a structural view of a film-forming equipment in this preferred embodiment. In this embodiment, by using atomicity hydrogen elements generated from the plasma composed of a mixed gas of helium gas and hydrogen gas, a platinum (Pt) film containing a high concentration hydrogen elements is formed on a platinum substrate. In Fig. 1, numeral "1" depicts a vacuum vessel. Into the vacuum vessel 1 are introduced a mixed gas composed of hydrogen gas and helium gas through a flexible tube 2. The mixed gas is excited to a plasma state in a quartz tube 4 with a microwave cavity 3. The quartz tube 4 with the microwave cavity 3 may be attached at a flange 5 in the right hand of the vacuum vessel 1. A spectroscope 6 attached to the opposite side to the flange 5 of the vacuum tube 1 can analyze the light emission in the plasma. A platinum plate as a substrate 7 is set and fixed onto a heating holder 8 in the vacuum vessel 1.

First of all, the interior of the vacuum vessel 1 is evacuated to a pressure of 1×10^{-5} Torr and below by a pump 100. Then, by heating the heating holder 1, the substrate 7 is heated to 300°C. The mixed gas of the helium gas and the hydrogen gas is introduced into the vacuum vessel 1 through the quartz tube 4 to a pressure of 1 Torr. The mix ratio of the

helium gas and the hydrogen gas is 1:1. Subsequently, the microwave of 2.45 GHz and 100 W is introduced into the quartz tube 4 through the microwave cavity 3. The thus generated atomicity hydrogen elements are supplied to the platinum substrate to form a platinum film containing a high concentration hydrogen elements on the platinum substrate.

The above film-forming process will be explained in detail, hereinafter. Fig. 2 is a view explaining the process in which the plasma energy is consumed for the atomicity of the hydrogen molecular elements. In Fig. 2, the excited level of the helium gaseous molecule is higher than the ground level thereof by 19.82 eV. On the other hand, the hydrogen molecular elements get the energy of about 19 eV to dissociate themselves in their atomicity-elements. The dissociated atomicity hydrogen elements having their excited states emit vacuum ultraviolet rays of 121.6 nm to be atomicity hydrogen elements having their ground states. In the case that the plasma has the helium gas molecules by the number equal to or more than the hydrogen molecular elements, as in this embodiment, the hydrogen molecular elements get the energies from the excited helium gas molecules to dissociate themselves into atomicity hydrogen elements. However, in the case that the plasma has only hydrogen molecular elements, the elements are directly excited and the atomicity hydrogen elements are almost never generated.

Fig. 3 shows the state in which the atomicity hydrogen elements are effectively generated from the plasma of the mixed gas of the helium gas and the hydrogen gas. In Fig. 3, the emission spectra are measured by the spectroscope 6. Compared with the emission spectrum of the plasma having only the hydrogen molecular elements, the emission spectrum has a large peak at a wavelength of 121.6 nm and a small peak around a wavelength of 160 nm which exhibits the molecular state-excitation of the hydrogen molecular element.

[A preferred second embodiment in the present invention]

The forming method of an insulating film according to the present invention will be described, with reference to Fig. 4. Herein, the similar parts in Fig. 4 to ones in Fig. 1 are designated by the same numerals. In this embodiment, a film made of a SiOF low dielectric constant material is formed for passivating aluminum (Al) wires on an insulating film. In Fig. 4, numeral "9" designates a vacuum vessel. Plasma-generating apparatuses 10, 11, and 12 are attached to the vacuum vessel 9, each apparatus having a flexible tube 2, a microwave cavity 3 and a quartz tube 4 which are combined. Then, as in Fig. 1, a spectroscopy 13, a substrate 14 and a heating holder 15 are provided.

First of all, the vacuum vessel 9 is evacuated to a pressure of 1×10^{-4} Torr and below by a pump 100. And by heating the heating holder 15 to 200°C, the substrate 14 is heated. The substrate has exposed aluminum wires by patterning an insulating film over the wires. A mixed gas of silane (SiH_4) gas and argon (Ar) gas, a mixed gas of oxygen (O_2) gas and xenon (Xe) gas and a mixed gas of fluorine (F_2) gas and krypton (Kr) gas are introduced into the plasma-generating apparatuses 10, 11 and 12, respectively. Then, the microwaves of 2.45 MHz and 100 W are introduced into the plasma-generating apparatuses to generate plasmas composed of the above mixed gases therein. The thus obtained atomicity silicon elements, atomicity oxygen elements and atomicity fluorine elements are supplied onto the substrate to form a SiOF film having a low dielectric constant. The composition of the SiOF film can be controlled by adjusting the ratio of the above atomicity elements.

[A preferred third embodiment in the present invention]

In this embodiment, the forming method of a ferroelectric film according to the present invention will be described hereinafter. Fig. 5 is a

film-forming equipment for the ferroelectric film in this embodiment. In this embodiment, a film made of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ferroelectric oxide is formed on an underfilm composed of a platinum/magnesium oxide (MgO) stacking structure. In Fig. 5, numeral "16" designates vacuum vessel and numeral "17" designates plasma-generating apparatus. Herein, the similar parts in Fig. 5 to ones in Fig. 1 are designated by the same numerals. A substrate 18 having the platinum/magnesium oxide stacking structure is set onto a heating holder 19 in the vacuum vessel 16. And three gas inlets 20 are provided in the side of the vacuum vessel 16.

The interior of the vacuum vessel 16 is evacuated to a pressure of 1×10^{-5} Torr and below by a pump 100. Under the vacuum condition, by heating the heating holder 19, the substrate 18 is heated to 450°C . Into the vacuum vessel 16 from the gas inlets 20 are introduced tetraethyl lead ($\text{TEL}:\text{Pb}(\text{C}_2\text{H}_5)_4$) gas, zirconium tetratertiarybutoxide ($\text{BOZ}:\text{Zr}(\text{t-OC}_4\text{H}_9)_4$) gas and titanium tetraisopropoxide ($\text{POT}:\text{Ti}(\text{i-OC}_3\text{H}_7)_4$) gas, as raw material gases. Moreover, as an oxidizing gas, a mixed gas of neon (Ne) gas and oxygen gas are introduced into the vacuum vessel 16 through the plasma-generating apparatus 17. The atomicity oxygen elements generated from the plasma composed of the mixed gas and the above raw material gases are reacted in the vacuum vessel 16 to form a $\text{Pb}(\text{Zr,Ti})\text{O}_3$ film on the substrate 18. Compared with the plasma composed of only the oxygen gas, the plasma composed of the mixed gas improves the oxidization of the film. [A preferred fourth embodiment in the present invention]

In this embodiment, the forming method of a semiconductor compound film will be explained. Fig. 6 shows a film-forming equipment in this embodiment. In this embodiment, a film made of gallium nitride (GaN) is formed on a substrate made of sapphire (Al_2O_3). In Fig. 6, numeral "21" designates a vacuum vessel and numeral "22" designates a plasma-

generating apparatus. Herein, the similar parts in Fig. 6 to ones in Fig. 1 are designated by the same numerals. The Al_2O_3 substrate 23 is set onto a heating holder 24 in the vacuum vessel 21. Moreover, a gas inlet 25 is provided on the vacuum vessel 21.

The interior of the vacuum vessel 21 is evacuated to a pressure of 1×10^{-5} Torr and below by a pump 100. Under the vacuum condition, the Al_2O_3 substrate 23 is heated through heating the heating holder 24. Then, gallium gas as a raw material gas is introduced from the gas inlet 25. Nitrogen gas as the other raw material gas is mixed with helium gas and the nitrogen molecular elements are excited into atomicity nitrogen elements in the plasma-generating apparatus 22 with the microwave of 2.45 MHz and 100 W. By using the atomicity nitrogen elements generated from the nitrogen molecular elements (which are almost never dissociated), the GaN film and a buffer layer for the film can be formed at a lower temperature than in the past.

[A preferred fifth embodiment in the present invention]

In this embodiment, the forming method of an amorphous semiconductor film according to the present invention will be explained. In this embodiment, the same film-forming equipment as the one in the first embodiment is used. In this embodiment, an amorphous silicon film for a solar battery is formed on a transparent electrode film formed on a glass substrate. Thus, in this embodiment, the substrate 7 in Fig. 1 is composed of the glass substrate and the transparent electrode film.

The interior of the vacuum vessel 1 is evacuated to a pressure of 1×10^{-5} Torr and below by a pump 100. Under the vacuum condition, by heating the heating holder 8, the substrate 7 having the transparent electrode film/glass substrate stacking structure is heated to 300°C . Silane gas as a raw material gas is diluted with argon gas by five times amount of the silane

gas, and is introduced into the vacuum vessel 1 through the quartz tube 4 to a pressure of 1 Torr. The microwave of 2.45 MHz and 100 W is introduced into the quartz tube 4 through the microwave cavity 3 to generate the plasma composed of the silane gas and the argon gas. The argon gaseous molecules absorb almost the plasma energy and thereby, the silane gaseous molecules get the energies (11.6 eV) from the excited state-argon gaseous molecules. Consequently, the silane gaseous molecules are dissociated into the atomicity silicon elements and thereby, the amorphous silicon film having good qualities is formed.

[A preferred sixth embodiment in the present invention]

In this embodiment, the forming method of a passivation film will be explained. Fig. 7 shows a film-forming equipment in this embodiment. In this embodiment, a film made of silicon oxide (SiO_2) is formed for passivating aluminum wires formed on an insulating film. In Fig. 7, numeral "26" designates a vacuum vessel and numerals "27" and "28" designate plasma-generating apparatuses. Herein, the similar parts in Fig. 7 to ones in Fig. 1 are designated by the same numerals. A substrate 29 composed of the insulating film and the patterned aluminum wiring structure formed on the insulating film is set onto a heating holder 30 installed in the vacuum vessel 26.

First of all, the interior of the vacuum vessel 26 is evacuated to a pressure of 1×10^{-5} Torr and below by a pump 100. Under the vacuum condition, by heating the heating holder 30, the substrate 29 is heated to 300°C . Then, silane gas is diluted with argon gas by five times amount of the silane gas, and the plasma composed of the silane gas and the argon gas is generated in the plasma-generating apparatus 27. Consequently, as in the fifth embodiment, the silane gaseous molecules are dissociated into the atomicity silicon elements, which are introduced into the vacuum vessel 26.

In the same way, oxygen gas is diluted with the krypton gas by the twenty time amount of the oxygen gas and the thus obtained mixed gas is introduced into the plasma-generating apparatus 28. Consequently, the atomicity oxygen elements are generated from the oxygen molecular elements and thereby, the SiO_2 film is formed on the substrate 29. Herein, the pressure in the vacuum vessel was 1 Torr. By the same manner, a film made of silicon nitride film can be formed from the atomicity silicon elements and the atomicity nitrogen elements generated from a mixed argon-silane gas and a mixed helium-nitrogen gas.

[A preferred seventh embodiment in the present invention]

In this embodiment, the method of effectively dissociating molecular elements into their atomicity elements will be described. In this embodiment, the same equipment as the one in the first embodiment is used. In this embodiment, hydrogen molecular elements are effectively dissociated into their atomicity hydrogen elements. Fig. 8 shows the emission spectrum of the atomicity hydrogen elements in the plasma composed of a mixed gas of helium gas:hydrogen gas=25:1. Then emission spectrum is measured with the spectroscopy 6. Compared with the plasma composed of a mixed gas of helium gas:hydrogen gas=1:1, the plasma composed of the mixed gas of helium gas:hydrogen gas=25:1, that is, having a larger amount of helium gas than hydrogen gas, exhibits an extremely large peak at a wavelength of 121.6 nm and extremely small peak around a wavelength of 160 nm. The dissociating method in this embodiment can be adopted for the first through fourth embodiments, so the oxygen molecular elements, the fluorine molecular elements and the nitrogen molecular elements can be effectively dissociated onto their atomicity elements.

[A preferred eighth embodiment in the present invention]

In this embodiment, the method for forming a P-doped silicon area

will be explained. In this embodiment, the same equipment as the one in the first embodiment is used. In this embodiment, a silicon substrate having a patterned insulating film with openings in a source area and a drain area is employed as the substrate 7 in the first embodiment.

First of all, the interior of the vacuum vessel 1 is evacuated to a pressure of 1×10^{-5} Torr and below by a pump 100. Under the vacuum condition, by heating the heating holder 8, the substrate 7 is heated to 500°C . P_2O_5 gas as a P-containing raw material gas is mixed with helium gas and the mixed gas is introduced into the vacuum vessel 1 through the quartz tube 4. The microwave of 2.45 GHz and 100 W is introduced into the quartz tube 4 through the microwave cavity 3 to generate the plasma composed of the mixed gas of P_2O_5 gas and helium gas. The helium gaseous molecules absorb almost the energies from the plasma and give the P_2O_5 molecular elements their excited energies. Accordingly, the P_2O_5 molecular elements are almost dissociated into their atomicity elements and thereby, the P-doped silicon area is formed at the openings of the substrate. Moreover, a boron (B) doped silicon area can be formed by using a mixed gas of B_2O_3 gas and neon gas instead of the above mixed gas.

[A preferred ninth embodiment in the present invention]

In this embodiment, the forming method of a boron-doped silicon film will be explained. In this embodiment, the same film-forming equipment as the one in the sixth embodiment is used. The substrate 30 is made of silicon material.

First of all, the interior of the vacuum vessel 26 is evacuated to a pressure of 1×10^{-5} Torr and below by a pump 100. Under the vacuum condition, by heating the heating holder 30, the substrate 29 is heated to 500°C . Then, B_2O_3 gas as a B-containing raw material gas is mixed to neon gas and the mixed gas is introduced into the plasma-generating apparatus 27.

Into the plasma-generating apparatus 28 is introduced a mixed gas of argon gas and silane gas. Thereafter, the atomicity boron elements and the atomicity silicon elements are generated from the mixed gases, respectively, and thus, the boron-doped silicon film is formed on the silicon substrate.

[A preferred tenth embodiment in the present invention]

In this embodiment, the forming method of a gate oxide film will be explained. In this embodiment, the same film-forming equipment as the one in the first embodiment is used. Moreover, in this embodiment, the substrate 7 is composed of the isolated silicon substrate shown in Fig. 10.

First of all, the interior of the vacuum vessel 1 is evacuated to a pressure of 1×10^{-5} Torr and below by a pump 100. Under the vacuum condition, by heating the heating holder 8, the isolated silicon substrate 7 is heated to 500°C. Then, argon gas and oxygen gas are introduced into the vacuum vessel 1 through the quartz tube 4 to a pressure of 1 Torr. In this case, the mixed gas has a ratio of the argon gas: the oxygen gas=25:1 and a flow rate of 100 sccm. The microwave of 2.45 GHz and 100 W is introduced into the quartz tube 4 through the microwave cavity 3 to generate the plasma composed of the mixed gas of the argon gas and the oxygen gas. The much argon molecules absorb almost the energies from the plasma and give the oxygen molecular elements the argon-excited energies. Consequently, the atomicity oxygen elements are generated from the oxygen molecular elements and react with the silicon elements constituting the silicon substrate to form a silicon oxide film at the opening of the silicon substrate 7. In this embodiment, the silicon substrate is oxidized at an oxidizing speed nearly equal to the one in the conventional 800°C-thermal oxidizing method using oxygen molecular elements.

[A preferred eleventh embodiment in the present invention]

In this embodiment, the film-forming method of oxidizing a silicon

substrate using krypton elements and oxygen elements will be explained. In this embodiment, the same film-forming equipment as the one in the first embodiment is used. Moreover, in this embodiment, the isolated silicon substrate shown in Fig. 10 is employed as the substrate 7 as in the tenth embodiment.

First of all, the interior of the vacuum vessel 1 is evacuated to a pressure of 1×10^{-5} Torr and below by a pump 100. Under the vacuum condition, by heating the heating holder 8, the substrate 7 is heated to 500°C . Then, the mixed gas of krypton gas: oxygen gas=25:1 is introduced at a flow rate of 100 sccm to a pressure of 1 Torr. The microwave of 2.45 GHz and 100 W is introduced into the quartz tube 4 through the microwave cavity 3 to generate the plasma composed of the mixed gas of krypton gas and oxygen gas. The krypton molecules absorb almost the energies from the plasma and give the oxygen molecular elements their excited energies (9.92 eV). Consequently, the oxygen molecular elements are almost dissociated into their atomicity oxygen elements and oxidize the opening of the isolated substrate 7. The thus obtained SiO_2/Si boundary face has a boundary face-level density of $3 \times 10^{11}/\text{cm}^2 \cdot \text{eV}$ at Dit (mid gap). Moreover, when the activation energy of the oxidizing reaction, which is an index of the diffusion rate controlling in the oxidizing reaction, is measured by varying the substrate temperature to 600°C from 300°C , it turns out to be about 0.14 eV. It means that the change of the oxidizing velocity to the change of the substrate temperature is extremely small. In this embodiment, the substrate temperature of 400°C gives the SiO_2/Si boundary face a boundary face-level density of $5 \times 10^{11}/\text{cm}^2 \cdot \text{eV}$ at Dit (mid gap).

[A preferred twelfth embodiment in the present invention]

In this embodiment, the film-forming method of oxidizing a silicon substrate using xenon elements and oxygen elements will be explained.

In this embodiment, the same film-forming equipment as the one in the first embodiment is used. Moreover, in this embodiment, the isolated silicon substrate shown in Fig. 10 is employed as the substrate 7 as in the tenth embodiment.

First of all, the interior of the vacuum vessel 1 is evacuated to a pressure of 1×10^{-5} Torr and below by a pump 100. Under the vacuum condition, by heating the heating holder 8, the substrate 7 is heated to 500°C . Then, the mixed gas of xenon gas: oxygen gas=25:1 is introduced at a flow rate of 100 sccm to a pressure of 1 Torr. The microwave of 2.45 GHz and 100 W is introduced into the quartz tube 4 through the microwave cavity 3 to generate the plasma composed of the mixed gas of xenon gas and oxygen gas. The thus generated atomicity oxygen elements enable the opening of the isolated silicon substrate 7 to be oxidized. In this embodiment using the plasma composed of the mixed gas of xenon and oxygen, an oxidizing velocity almost equal to that in the conventional 900°C -thermal oxidizing method can be obtained and the oxidation of the silicon substrate can be realized at a low temperature of 400°C .

[A preferred thirteenth embodiment in the present invention]

In this embodiment, the film-forming method of nitriding a silicon substrate using helium elements and nitrogen elements will be explained. In this embodiment, the same film-forming equipment as the one in the first embodiment is used. Moreover, in this embodiment, the isolated silicon substrate shown in Fig. 10 is employed as the substrate 7 as in the tenth embodiment.

First of all, the interior of the vacuum vessel 1 is evacuated to a pressure of 1×10^{-5} Torr and below by a pump 100. Under the vacuum condition, by heating the heating holder 8, the substrate 7 is heated to 600°C . Then, the mixed gas of helium gas: nitrogen gas=10:1 is introduced into the

vacuum vessel 1 through the quartz tube 4 at a flow rate of 100 sccm to a pressure of 1 Torr. A microwave of 2.45 GHz and 100W is introduced into the quartz tube 4 through the microwave cavity 3 to generate the plasma composed of the mixed gas of helium gas and nitrogen gas.

The thus generated atomicity nitrogen elements enable the opening of the isolated silicon substrate 7 to be directly nitrated.

[A preferred fourteenth embodiment in the present invention]

In this embodiment, the forming method for forming an oxynitride film (SiON film) will be described. In this embodiment, the same film-forming equipment as the one in the sixth embodiment is used. Moreover, in this embodiment, the isolated silicon substrate shown in Fig. 10 is employed as the substrate 7 as in the tenth embodiment.

First of all, the interior of the vacuum vessel 26 is evacuated to a pressure of 1×10^{-5} Torr and below by a pump 100. Under the vacuum condition, by heating the heating holder 30, the substrate 29 is heated to 600°C. Then, the mixed gas of krypton gas: oxygen gas=25:1 is introduced into the plasma-generating apparatus 27. And the mixed gas of helium gas: nitrogen gas =10:1 is introduced into the plasma-generating apparatus 28. In this case, the pressure in the vacuum vessel is 1 Torr. The atomicity oxygen elements and the atomicity nitrogen elements, generated in the plasma-generating apparatuses, react with the silicon elements constituting the silicon substrate to form the SiON film having a good boundary face quality and a high dielectric constant.

(Industrial Applicability)

According to the present invention, the molecules, each composed of plural atoms, can be effectively dissociated into their atomicity elements, the low temperature film-forming process, using the molecules, can be realized.

(Claims)

1. A film-forming method of supplying gaseous molecules, each composed of plural atoms, onto a substrate, wherein the plasma composed of the mixed gas of an inert gas and the gas containing the gaseous molecules is generated to excite the inert gaseous molecules, and the excited inert gaseous molecules having higher quasi-stable level energies than the ones requiring to dissociate the gaseous molecules into their atomicity elements are collided with the gaseous molecules to dissociate them into their atomicity gaseous elements to supply the elements onto the substrate.

2. A film-forming method as defined in claim 1, wherein the gaseous molecules are oxygen molecules.

3. A film-forming method as defined in claim 1, wherein the gaseous molecules are nitrogen molecules.

4. A film-forming method as defined in any one of claims 1 to 3, wherein the inert gaseous has a molecule density not less than that of the gaseous molecules in the mixed gas.

5. A film-forming method as defined in any one of claims 1 to 4, wherein the substrate is a silicon substrate and the gaseous molecules contains the constituting elements of a silicon compound to be film-formed onto the substrate.

6. A film-forming method as defined in claim 5, wherein at least a part of the silicon elements constituting the silicon compound are dissociated into the atomicity silicon elements.

7. A film-forming method as defined in claim 5, wherein the silicon compound is a silicon oxide.

8. A film-forming method as defined in claim 7, wherein the inert gas is krypton gas and the gaseous molecules are oxygen molecules to be dissociated into the atomicity oxygen element to oxidize the substrate.

9. A film-forming method as defined in claim 7, wherein the inert gas is xenon gas and the gaseous molecules are oxygen molecules to be dissociated into the atomicity oxygen elements to oxidize the substrate.

10. A film-forming method as defined in claim 5, wherein the silicon compound is a silicon nitride and the inert gas is helium gas, and the gaseous molecules are nitrogen molecules to be dissociated into the atomicity nitrogen elements to nitride the substrate.

11. A film-forming method as defined in claim 5, wherein the silicon compound is a silicon oxynitride.

00810 (PCT/JP99/01429)

(Abstract)

In a film-forming process of depositing gaseous molecules each composed of plural atoms onto a substrate or reacting the gaseous molecules with the constituting elements of the substrate to form a compound film onto the substrate, the plasma, having the excited inert gaseous molecules having higher quasi-stable level energies than the ones requiring to dissociate the gaseous molecules into their atomicity elements and the gaseous molecules, is generated and then, the gaseous molecules are dissociated into their atomicity elements before the depositing into the substrate. As a result, the dissociation of the gaseous molecules onto the substrate is not required, leading to the lowering of the film-forming process.

0094-3364-90

FIG. 1

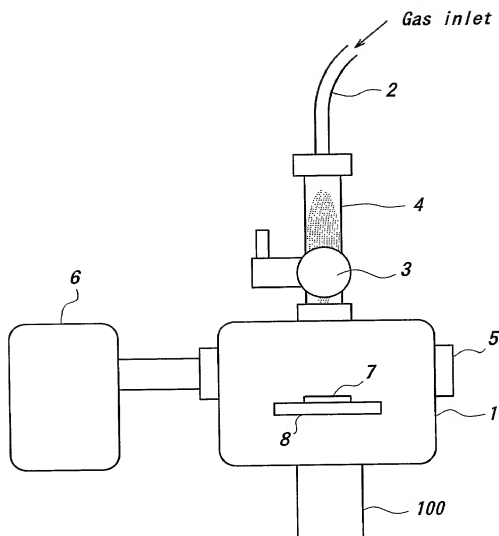


FIG. 2

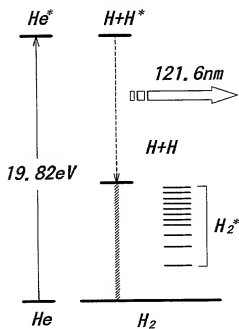


FIG. 3

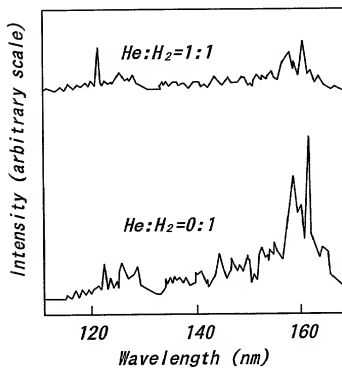


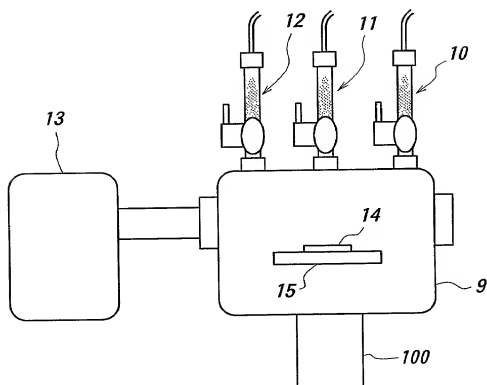
FIG. 4

FIG. 5

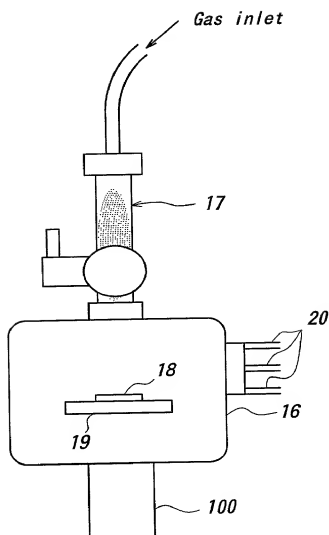


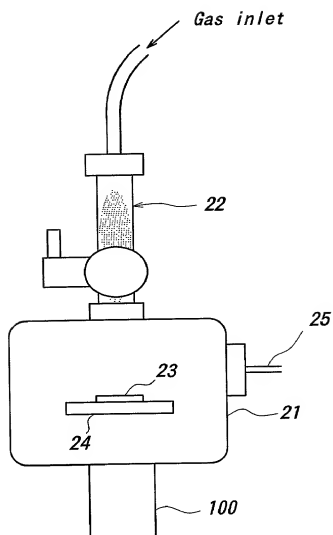
FIG. 6

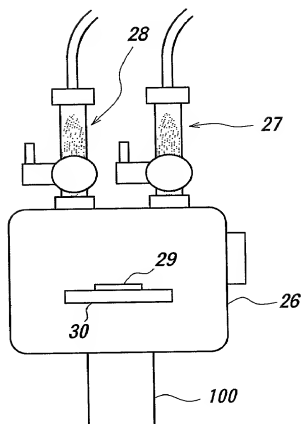
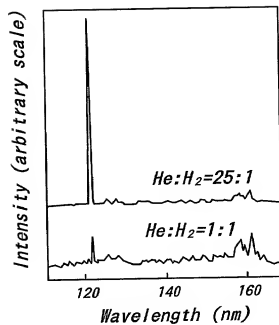
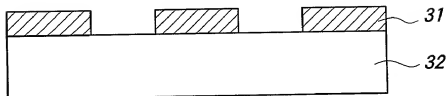
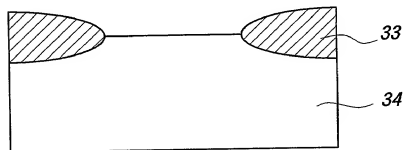
FIG. 7

FIG. 8**FIG. 9****FIG. 10**

Declaration and Power of Attorney
Under Patent Cooperation Treaty
35 USC §371(c)(4)

米国特許庁 (00210)

PCT/JPO99/01429

As a below named inventor, I hereby declare that:

my residence, post office address and citizenship are as stated below next to my name; that

I verily believe that I am the original, first and sole inventor (if only one name is listed below) or a joint inventor (if plural names are named below) of the invention entitled:

A METHOD FOR FORMING A FILM

described and claimed in the international application number PCT/JPO99/01429 filed March 23, 1999 and as amended on (if any), the specification and claims of which I have reviewed and understand and for which I solicit a patent.

I acknowledge my duty to disclose information of which I am aware which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a), and that no application for patent or inventor's certificate on this invention has been filed in any country foreign to the United States of America prior to my international application by me or my legal representatives or assigns, except as follows:

The priority of the above applications (if any), filed within a year prior to my international application is hereby claimed under 35 USC 119. I hereby appoint the following as my attorneys of record with full power of substitution and revocation to prosecute this application and to transact all business in the patent office:

Roger W. Parkhurst, Reg. No. 25,177; Charles A. Wendel, Reg. No. 24,453; Lawrence D. Eisen, Reg. No. 41,009.

ALL CORRESPONDENCE IN CONNECTION WITH THIS APPLICATION SHOULD BE SENT TO:
PARKHURST & WENDEL, L.L.P., 1421 PRINCE STREET, SUITE 210, ALEXANDRIA, VIRGINIA 22314-2805, TELEPHONE (703) 739-0220.

I hereby declare that I have reviewed and understand the contents of this Declaration, and that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

3. Full Name of Sole or First Inventor FED Tomo UENO
- | | Given Name | Middle Initial | Family Name |
|--------------------------|-------------|----------------|-------------|
| *4. Inventor's Signature | <u>Tomo</u> | | <u>UENO</u> |
- Date of Signature October 5, 2000
- | | Month | Day | Year |
|--|---|-------------------|--------------|
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| | City | State or Province | Country |
| 7. Citizenship | <u>Japanese</u> | | |
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| (Insert complete mailing address, including country) | <u>Tokyo 104-0051 JAPAN</u> | | |

*IF THERE IS MORE THAN ONE INVENTOR USE PAGE 2 AND PLACE AN "X" HERE ☐.